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CHEMISTRY OF ORGANIC SULFUR COMPOUNDS IN CRUDES AND PETROLEUM PR DUCTS

By Various Authors

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CHEMISTRY OF ORGANIC SULFUR COMPOUNDS IN CRUDES AND PETROLEUM PRODUCTS

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THE CORROSIVE PROPERTIES OF SULFUR-BEARING CRUDES

by

L.D.Zakharochkin and S.M.Vol'fson

(Giproneftemash)

Academician I.M.Gubkin, who for a long time headed all geological research connected with the prospecting, exploration, and development of oil and gas fields, when speaking of the problem of the expansion of crude oil production in the foothills of the Caucasus and in Central Asia, always emphasized the importance and timeliness of the problem of discovering new petroleum and gas-bearing deposits in the flatlands of the USSR.

The decision of the Party to establish the great oil base of the Second Baku in the region between the Volga and the Urals initiated an extensive development of the subsurface resources of the immense plains of the USSR. The expansion of the prospecting, exploration, and development of oil and gas fields in the Ural-Volga petroliferous region has led to the great growth of oil extraction in these regions.

Most of the crudes of the Ural-Volga petroliferous region are sulfur-bearing. The total sulfur content in the crudes of the Eastern oil fields of the USSR varies over a very wide range, from 0.3 to 4.5 wt.%. The sulfur in these crudes is mainly in the form of organic sulfur compounds, mercaptans, sulfides, disulfides, polysulfides, thiophenes and other compounds (Bibl.1). These types of sulfur compounds include numerous groups of sulfur compounds, whose differences are due to the alkyl groups bound to the sulfur. But we also find crudes that contain hydrogen sulfide

and elementary sulfur together with organic sulfur compounds.

In refining, the sulfur compounds in crudes and petroleum products undergo various transformations, as a result of which we have to do in practice, not only with natural sulfur compounds contained in the crudes but also with the products o these transformations.

M.G.Rudenko and V.N.Gromova (Bibl.2), while investigating the thermal stabili of several sulfur compounds, have shown that the mercaptans are the most stable of these sulfur compounds. The substitution of the hydrogen in the SH group by a rad cal, i.e., the conversion of mercaptans to sulfides, increased the thermal stabili of these compounds manyfold. Sulfides are distinguished by high thermal stability regardless of boiling point and class. It was also found that high thermal stability is characteristic of all sulfur compounds with sulfur in the ring.

Work on the catalytic transformations of sulfur compounds (Bibl.3-5) has show that catalysts act strongly both to lower the temperature at which the transformations of sulfur compounds begins and to increase the degree and depth of these transformations. The sulfur compounds here undergo various reactions (liberation hydrogen sulfide, hydrogenation, dehydrogenation, disproportionation of hydrogen). The direction of the reaction depends on the nature of the sulfur compounds, the type of catalyst, the temperature, etc. Mutual transformation of the sulfur compounds takes place during catalytic reactions, but ultimately all these processes proceed irreversibly toward the formation of hydrocarbons and liberation of sulfu in the form of hydrogen sulfide.

Some sulfur compounds contained in crudes (elementary sulfur, hydrogen sulfi mercaptans) and the transformation products formed during refining by organic sul compounds are sources of intense corrosion of refinery equipment.

Many years of USSR experience in refining sulfur-bearing crudes from various oil fields of the Soviet Union have shown these crudes to be of varying corrosive activity. The ability to evaluate the corrosive properties of sulfur-bearing cru

and their knowledge is important for practice, since the equipment of refineries and the cost of protecting it from corrosion is of course ruled by the aggressiveness of the crudes being refined. Until recently, there was no method in the USSR for evaluating the corrosive properties of sulfur-bearing crudes. During the first stages of large-scale refining of sulfur-bearing crudes, their aggressive properties were attributed to the total sulfur content, but it became obvious later that the total sulfur content in crudes from various oil fields could not serve as a criterion of their corrosive properties.

In this connection, an accelerated laboratory method of estimating the corrosive properties of crudes was developed at the State Institute for Petroelum Refinery Equipment. The method makes it possible to determine the direct indices of the corrosive activity of crudes distilled at temperatures up to 350°C under atmospheric pressure, and to determine the quantity of hydrogen sulfide liberated under these conditions. A detailed description of this method was presented in a paper before the Second Scientific Session devoted to the chemistry of organic sulfur compounds.

The principal results of work on the corrosive properties of sulfur-bearing crudes of a number of oil fields in the Kuybyshev and Orenburg Oblasts, and of Tartary and Bashkiria, are given in the Table. The experimental data have shown that a considerable group of specimens of sulfur-bearing crudes examined, containing 0.28 to 1.99% of sulfur exhibit low corrosive activity when subjected to atmospheric distillation up to 350°C, and approach the low-sulfur crude of the Baku region (Surakhan) in their corrosive properties. The quantity of hydrogen sulfide liberated on their distillation did not exceed 250 - 260 mg per liter of crude, and the rate of corrosion of carbon steel due to these crudes did not exceed 0.5 mm/year.

With increasing amount of hydrogen sulfide liberated on distillation an increased corrosive activity of the crudes is also noted. In cases where the amount of hydrogen sulfide liberated was 400 - 600 mg/ltr of crude, the rate of corrosion

of carbon steel rose to 0.8 - 1.0 mm/year, and at 600 - 1000 mg/ltr crude it reached 1.7 - 2.3 mm/year.

The crudes examined also included sulfur-bearing specimens with very high corrosive activity, which yielded 1600 to 9500 mg of H_2S per liter of crude on distillation, and showed a rate of carbon steel corrosion amounting to 2.5 - 6.8 mm/year.

The experimental data show that an extensive group of crudes from the Ural-Volga petroliferous region, which are usually grouped together under the common designation of "sulfur-bearing crudes" do in fact include crudes with sharply differing corrosive properties. As the petroleum industry developed in the regions between the Volga and the Urals, the variety of the crudes has increased year by year.

Corrosive Properties of Sulfur-Bearing Crudes

Crude	Petroliferous Horizon	Well No.	Date of Sample, Month and Year	ρ_4^{20}	Kinematic Viscosity, ν_{20}	Sulfur (by Bomb Method) wt, %	Hydrogen Sulfide Liberated on Distillation up to 350°C, mg/ltr of Crude	Rate of Corrosion of Carbon Steel at 350°C, mm/year
Surakhany* (Baku)	-	—	--	0,8490	11,13	0,08	49	0,34
Mukhany	Devonian, seam III	68	V-56	0,8200	5,81	0,28	39	0,14
Mukhany	Devonian, seam II	38	V-56	0,8420	7,32	0,77	44	0,16
Shkapov	Devonian, seam IV	15	VII-56	0,8175	5,32	0,59	56	0,15
Dmitriyev	Devonian	21	V-56	0,8360	6,28	1,05	70	0,22
Mikhaylov	Carboniferous suite, seam IV	22	V-56	0,8200	5,38	0,66	70	0,26
Zol'nyy	Devonian	54	V-56	0,8040	3,21	0,76	130	0,28
Mikhaylov	Carboniferous suite, seam II	26	V-56	0,8345	8,90	0,97	150	0,38
Pokrovsk	Carboniferous suite suite	19	V-55	0,8540	14,58	1,15	156	0,41
Mukhany	Carboniferous suite, seam III	23	V-56	0,8545	15,54	1,67	178	0,32
Zhigulevsk	Devonian	6	V-56	0,8475	8,47	1,52	190	0,36
Serafimov	Devonian, seam I	210	VII-56	0,8395	8,36	1,03	160	0,26
Serafimov	Devonian, seam IV	217	VII-56	0,8250	5,83	0,85	215	0,29
Serafimov	Devonian, seam II	290	VII-56	0,8263	9,51	0,86	178	0,56
Romashkin**	Devonian	—	--	0,8760	29,59	1,52	198	0,49

(Table Continued)

Crude	Petroliferous Horizon	Well No.	Date of Sample, Month and Year	ρ_4^{20}	Kinematic Viscosity, ν_{20}	Sulfur (by Bomb Method) wt, %	Hydrogen Sulfide Liberated on Distillation up to 350°C, mg/1tr of Crude	Rate of Corrosion of Carbon Steel at 350°C, mm/year
Tarkhany	Devonian	127	V 56	0,8810	26.41	1.90	215	0.46
Shkapov	Devonian, seam I	62	VII 56	0,8625	15.80	1.67	263	0.39
Mukhany	Carboniferous, suite, seam IV	19	V 55	0,8588	17.39	1.58	403	0.87
Tuymazy**	Devonian			0,8490	10.22	1.29	490	0.94
Pokrovsk	Bashkirian stage	10	V 55	0,7990	3.34	0.56	580	0.94
Sultangul**	Devonian		-	0,8904	47.91	1.78	585	1.06
Mukhany	Carboniferous suite, seam I	19	V 55	0,8391	8.88	1.10	529	1.92
Zol'nyy	Carboniferous suite	83	V -56	0,8370	6.68	1.39	673	1.69
Strel'na	Carboniferous suite	18	V 56	0,8510	10.60	1.66	1038	1.77
Tarkhany	Carboniferous suite	124	V 56	0,8745	21.26	3.10	1003	2.26
Yablonyy	Kungurian stage, seam I	269	V -55	0,8536	10.47	2.0	2525	2.56
Baytugan**	Carboniferous suite	—	—	0,8968	54.19	2.58	1745	3.12
Radayevsk	Carboniferous suite, horizon B-2	16	V 55	0,8978	81.06	3.05	1600	3.77
Sernovodsk	Carboniferous suite, horizon B-2	7	V 55	0,8934	50.03	3.41	2587	3.5
Starokazan	Artinian stage	48	VII -56	0,8680	17.78	2.50	2435	5.2
Ishimbay	Artinian stage	77.1	VII -56	0,8745	19.0	3.12	5381	6.89
East Stepanovsk	Kalino suite	30	V -55	0,8720	17.28	2.94	6495	5.44
Kalino	Seam of upper Permian deposits	390	V -55	0,8930	30.80	3.80	9500	6.25

*Specimen of crude obtained at Petroleum Institute, Academy of Sciences USSR.
**Specimens of crude obtained at All-Union Petroleum Industry Research Institute.

Besides the highly aggressive crudes of Ishimbay, Syzran, Kinel', Stavropol' and Buguruslan, which were the principal crudes refined between 1936 and 1944, new

oil fields have been discovered and put into production during the last 10-12 yea yielding crudes differing sharply in their total sulfur content and in their corr sive properties. Further than that, not only new oil and gas-bearing areas were developed, but also new productive strata. For instance, such a new stratum whic yielded crude soon after the war and opened up a new stage in the development of oil production in the regions between the Volga and the Ural were the Devonian de posits. Devonian oil was discovered in Western Bashkiria on the Samara Luke, nea Saratov, in Tartary, and in other areas of the Ural-Volga region. The sulfur con tent in the crudes from the Devonian horizons does not exceed 1.5 - 1.6%, and in number of cases it is as low as 0.8 - 1.0%. The Devonian crudes contain sulfur c pounds of higher thermal stability, and are unaggressive when distilled up to 350

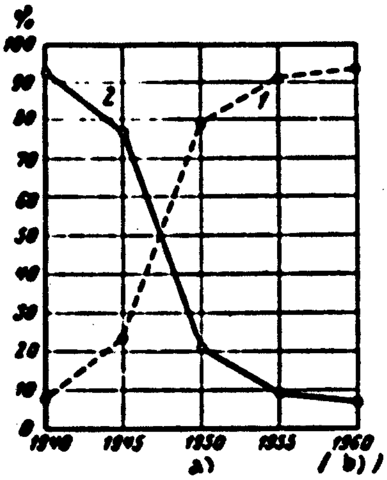
Considerable quantities of crudes being produced today are from the Carbonif ous deposits, with low sulfur and only slight corrosive activity. Such Carbonife ous crudes include those from Mykhany, Mikhaylov, and Pokrovsk.

The figure shows data characterizing the pattern of growth of the production both highly aggressive and weakly aggressive crudes in the Ural-Volga region. The highly aggressive crudes include those from Staro-Ishimbay, Vvedenovsk, Starokaza Tuymazy Carboniferous suite, Shugura, the crudes produced by the Kinel'neft' Trust (Zol'ny, Strel'ny, Yablony Gorge, Carboniferous suite), the crudes of the old are of the Syzran region, the crudes produced by the Pervomaysk-Chernovsk Trust, the crudes from the Radayevsk Consolidated Oilfields, and the crudes produced by the Buguruslanneft' Combine.

The low-corrosion crudes include those from Bashkiria, Tatary, and Kuybyshev Oblast, some crudes from Carboniferous deposits, with relatively low sulfur, exhit ing only slight corrosive properties, and the crudes from Saratov and Stalingrad Oblasts.

The data in the figure show that in 1940 the crudes produced in the Ural-Volg region consisted mostly of high-sulfur and highly aggressive crudes (92.2%). Late

beginning in 1944 - 1945, the contribution of the highly aggressive crudes to the total oil production in these regions fell sharply, in 1945 it was 76.6%, in 1950 20.9%, in 1955 9.0%. Allowing for the prospective development of the individual



Contribution of Low-Aggressive and High-Aggressive Crudes to Crude Oil Production in the Ural-Volga Petroliferous Region:

1 - Low-aggressive; 2 - High-aggressive

a) Year; b) Plan

oil-bearing regions, it is calculated that in 1960 the contribution of the highly aggressive crudes will be about 6.5%.

The changes that have taken place in the pattern of the properties of the crudes produced in the Ural-Volga region (we mean the corrosive, aggressive properties of the crudes) advance the problem of organizing the rational and separate collection, storage, transportation, and refining of a wide range of sulfur-bearing crudes. We are very clear about the fact that these questions must be solved not only with respect to the corrosive properties of the crudes, but also with respect to the other physical and chemical properties of the crudes, the directions of the refining process, the geography of oil-field and refinery location, allowing for the existing means of transportation, etc.

In spite of the difficulties in the way of organizing a rational and separ collection and refining of the eastern crudes, we must still recognize the imper-tive necessity of such separation, and the work undertaken in this direction by petroleum industry must be decisively continued and expanded.

The propositions about the organization of rational collection and refinin the crudes of the Ural-Volga region should in our opinion be worked out by the Councils of National Economy of Tartary, Bashkiria and Kuybyshev Oblast with th participation of a number of research institutes of the petroleum industry, and should be reviewed and approved by the higher-echelon directive organizations.

At the same time, we also consider it possible and expedient, even today, note certain priority measures which result from an analysis of the existing situation.

1. Up to now oil fields have appeared where it has become necessary to est lish conditions for the separate collection of crudes. Such oil fields include those of Tuymazy, Mukhan and Shkapov.

2. Since it has become the practice to concentrate the refining of the mos aggressive sulfur-bearing crudes at three refineries - Kuybyshev, Syzran and Ishimbay - it is expedient to concentrate all the refining of crudes of this ty these refineries, and to permit no deliveries of aggressive crudes to any other fineries whatsoever, to say nothing of refineries not equipped to handle sulfur bearing crudes (Gur'yev, Orsk, Groznyy, etc.).

3. It is imperative to work out measures and put them into effect graduall over a short period (1 - 1.5 year) to adapt the equipment and the individual el ments of the general plant installations at the Kuybyshev, Ishimbay, and Syzran fineries to handle highly aggressive sulfur-bearing crudes, in order to effect maximum reduction in the extent of corrosion and the amount of repair and rebui work at these refineries.

Conclusions

1. The results of this work have shown that an extensive group of crudes of the Ural-Volga region, usually lumped together under the common designation of "sulfur-bearing crudes", in fact include crudes differing sharply in corrosive properties when distilled under atmospheric pressure up to 350°C.

2. The changes that have taken place in the pattern of the properties of crudes produced in the Ural-Volga region (with respect to their corrosive properties) insistently demand a decisive continuation and expansion of the efforts taken by the industry to organize the separate collection and refining of a wide assortment of crudes of the Ural-Volga region.

3. It is necessary to introduce into the practice of the analysis of the crudes from new oil fields and horizons a determination of their aggressive properties by the developed method in order, on the one hand, to determine the rational points for refining such crudes and, on the other hand, in building refineries, to provide the most correct and economically advisable measures to protect the equipment from corrosion, according to the degree of aggressiveness of the particular crudes involved.

4. The work on development of a method or estimating the aggressiveness of sulfur-bearing crudes and petroleum products under the conditions of high-temperature processes (thermal and catalytic cracking) should be continued.

* * *

Junior Scientists S.T.Meshcheryakov and N.V.Tokareva, and Laboratory Assistants O.V.Kalinina and G.G.Zhukova, participated in the experimental part of this work.

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THE CORROSIVE PROPERTIES OF FUELS PRODUCED FROM SULFUR-BEARING CRUDES

by

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With the widespread introduction of fuel TS-1, produced from sulfur-bearing crudes and therefore containing up to 0.25% sulfur, the various consumers became concerned about its possible corrosive action on fuel-feed systems.

From the literature data, referring primarily to fuels for carburetor engines, we know of the corrosive action of active sulfur compounds, including hydrogen sulfide, elementary sulfur, and mercaptans, on various engine parts (Bibl.1).

According to the production technology of TS-1 and T-2 fuels that has been adopted at the various plants, these fuels are now completely free of hydrogen sulfide.

As for their content of elementary sulfur, this element has been detected in several commercial batches of TS-1 in amounts not exceeding 0.001 - 0.002%. The total mercaptan sulfur in fuels TS-1 and T-2, produced from sulfur-bearing crudes, does vary within a wide range (0.005 - 0.3%).

The presence of mercaptans in TS-1 fuel has made it necessary to study the corrosive action of these fuels on the various parts of the fuel system in turbojet

engines, and to establish standards for the permissible content of mercaptan sulfur in such fuels.

The corrosive properties of the fuels were determined from the weight loss of a metal strip after immersion of 100 hrs in the fuel, at 60°C. Earlier joint studies by the Research Institute for Petroleum Industry and the VIAM had established that

Table 1

Corrosiveness of Turbojet Fuels Produced from Sulfur-Bearing Crudes, as a Function of their Content of Mercaptan Sulfur

(Tests on Copper and Bronze VB-24)

Fuel	Original Fuel		Copper		Bronze VB-24	
	Sulfur Content, %					
	Total Sulfur	Mercaptan Sulfur	a)	Weight Loss of Strip, gm/m^2	a)	Weight Loss of Strip, gm/m^2
TS-1	0,12	Absent	Absent	Absent	Absent	Absent
"	0,14	0,002	"	0,6	"	1,4
"	0,15	0,005	--	—	"	3,3
"	0,17	0,010	--	--	"	6,8
"	0,18	0,025	0,024	0,3	0,015	9,3
"	0,30	0,050	0,050	0,5	---	10,8
T-2	0,14	0,002	Absent	0,8	Absent	1,1
"	0,15	0,005	0,001	2,5	"	3,5
"	0,15	0,010	0,008	3,1	"	7,6
"	0,17	0,025	0,015	6,2	0,014	12,3
"	0,23	0,050	0,038	9,3	0,024	14,2

a) Mercaptan Sulfur Content of Fuel after Test, wt.%

fuel TS-1, with a mercaptan sulfur content up to 0.05%, had no corrosive action on several metallic materials used for parts of the fuel system of turbojet engines: bronze Br AZhN-10-4-4, aluminum alloys, and steel. A detailed study of the corrosiveness of various samples of fuels TS-1 and T-2 produced from sulfur-bearing crudes was conducted with materials most sensitive to the corrosive action of mercaptans: bronze VB-24 and copper.

The investigation was made on samples of fuels TS-1 and T-2 containing 0.002 0.05% of mercaptan sulfur. Commercial and experimental samples of the fuels were

gelatinous deposits on the springs and a sharp decrease in the mercaptan sulfur content of the fuel. The chromate passivation of the cadmized springs exerted a protective action but did not completely prevent the formation of the gelatinous deposit on the springs when tested in this fuel.

Fuel TS-1, containing 0.01% mercaptan sulfur, causes no formation of gelatinous

Table 4

Weight Loss of Cadmized Springs (gm/m^2) during the Test

Fuel	Mercaptan Sulfur Content of Original Fuel, %	Test Conditions for Cadmized Springs					
		Unpassivated			Passivated		
		a)	In Fuel Over a Water Cushion	In Fuel Shaken with Water	a)	In Fuel Over a Water Cushion	In Fuel Shaken with Water
TS-1 (GOST 4138-49)	0,002	0,97	4,10	3.44	absent	0,23	0,90
TS-1		absent	absent	absent	absent	absent	absent
TS-1	0,01	-	27,00	40,00	0,70	3,83	9,26
TS-1	0,026	8,44	106,60	106,77	9,62	13,57	71,83
T-2	0,011	1,66	6,01	35,52	0,9	0,38	1,20

a) In unmoistened fuel

deposits in tests on cadmized springs in unwatered fuel, and very small amounts of deposits in tests in fuel watered by shaking with water.

The loss of weight of passivated cadmized springs tested in this fuel is extremely slight, and the content of mercaptan sulfur in the fuel remains practically unchanged.

Thus, under rather severe test conditions, when cadmized springs are tested in TS-1 fuel containing 0.01% mercaptan sulfur, chromate passivation of the springs reliably protects the cadmium coating and prevents the formation of gelatinous deposits even when the fuel is strongly moistened (fuel with suspended water). Under the test conditions, the corrosiveness of fuel T-2, with 0.01% mercaptan sulfur, is similar to that of fuel TS-1 with the same mercaptan sulfur content. In tests with

It will be seen from Table 2 that, under the test conditions adopted, copper is considerably corroded by the fraction boiling in the range 60 - 130°C and very little corroded by the 130 - 240°C fraction.

Thus the increased corrosiveness of fuel T-2 for copper may be explained by t

Table 2

Corrosiveness of Fractions with Boiling Ranges of 60 - 130 and 130 - 240°C, of Straight-Run Products of Sulfur-Bearing Crudes, as a Function of their Content of Mercaptans

Boiling Range of Fraction, °C	Mercaptans in Original Fuel, wt. %	Copper	
		Mercaptans Content of Fuel after Test, wt.%	Weight Loss of Strip, gm/m^2
60 - 130	0,001	Absent	0,50
	0,005	"	2,80
	0,015	"	7,80
	0,025	"	10,60
	0,045	0,015	14,90
130 - 240	0,001	Absent	0,40
	0,005	0,003	0,40
	0,015	0,012	1,30
	0,025	0,017	1,80
	0,045	Not determined	3,10

considerably higher corrosivity of the low-molecular mercaptans contained in fuel T-2 by comparison with the mercaptans in fuel TS-1.

As already mentioned, fuel TS-1, manufactured in the plant installations, som times contains slight amounts of elementary sulfur.

Special experiments made with test samples, to which various amounts of elementary sulfur had been added, showed that the presence of elementary sulfur up tc 0.002% in the fuel, i.e., in amounts that could not be detected by the copper-stri test (GOST 6321-52), do not increase the corrosive action of fuel TS-1 with 0.018% mercaptans on bronze VB-24. With respect to copper, the corrosive action of fuel TS-1 containing mercaptans is sharply intensified on addition of elementary sulfur to the fuel. On addition of 0.001% of elementary sulfur to the fuel, the weight

loss of the copper strip after 100 hr of test increased from 0.5 to 9 gm, i.e., by a factor of 18. Here there was a considerable decrease in the mercaptan sulfur of the fuel.

It is of great practical importance to elucidate the character of the corrosion of metals in sulfur-bearing fuels, as a function of the contact time. With this object, we ran experiments on the corrosion of copper and bronze VB-24 in fuel TS-1 and T-2 with varying amounts of mercaptans at varying test durations. Figure 3 gives the results of the tests.

It will be seen from the data in Table 3 that, at the test temperature of 60°C, bronze VB-24 begins to undergo corrosion in fuels TS-1 and T-2 almost from the instant of immersion in the fuel. The mercaptan content decrease is simultaneous with the weight loss of the strip in the fuel. The corrosion of a strip of bronze VB-24 under test conditions in fuels TS-1 and T-2 with up to 0.015% mercaptans ended after 100 hrs, while in the fuels containing from 0.025 - 0.050% mercaptans, it ended after 150 hrs; during this period, the mercaptans contained in the fuels were completely used up.

Under similar test conditions, the interaction of the mercaptans in fuel T-2 (and especially in fuel TS-1) with the copper strip is considerably slower.

The results of the experiments show that the corrosion of bronze VB-24 does not so much depend on the amount of mercaptans in the fuel as on the contact time between the bronze and the fuel. During the first 25 hrs of the tests, the corrosion of bronze VB-24 was slight, and was practically the same for all fuels with mercaptan contents of 0.004 - 0.05%. This may explain the observation that under operating conditions, when fuel is continually being pumped through the fuel pumps, the corrosion of the bronze parts is slight and is practically the same for TS-1 fuels with 0.002 and 0.026% mercaptans.

The cadmized parts of the fuel system proved more sensitive to the action of mercaptan sulfur. Under engine operating conditions, in regions with elevated at-

mospheric humidity, the formation of gelatinous deposits on the cadmized surface of pump parts was noted, which in some cases interfered with operation of the fuel pumps.

To elucidate the causes and conditions of formation of these deposits in operating with fuels produced from sulfur-bearing crudes, the appropriate laboratory tests were run on industrial samples of fuel TS-1 containing 0.01 and 0.025% mercaptan sulfur and fuel T-2 containing 0.01% mercaptan sulfur. For comparison we also ran tests on fuels free of mercaptan sulfur: fuels T-1 and fuels TS-1 from sulfur-bearing crudes that had first been treated with sodium plumbite. The series-produced steel springs, cadmized both unpassivated and after chromate passivation were also tested for corrosion by these fuels.

The test of the cadmized springs for corrosion was run at room temperature for 50 days, changing the fuel every 10 days, with complete immersion of the springs in the fuel. To elucidate the effect of increased moisture content of the fuel on the rate of formation of the gelatinous deposits on the cadmized parts, corrosion tests on the springs were run at various moisture contents of the TS-1 and T-2 fuels.

1) Unwatered fuel;

2) Fuel watered by storage over a water cushion;

3) Fuel watered by shaking with distilled water, followed by storage over a water cushion.

The corrosive action was estimated from the weight loss of the springs, from the change in their appearance, and from the change in the mercaptan content of the fuel. Particular attention was paid to the time of first appearance of the gelatinous deposits on the springs, and to the amount of such deposits. Table 4 gives data on the weight loss of the springs.

As will be seen from these data, the greatest weight loss was noted for the unpassivated springs, tested in the fuel containing 0.025% mercaptan sulfur and watered by shaking with water. In this case, we noted the formation of extensive

Table 3

Corrosive Action of Fuels T-1 and T-2 on Metals, as a Function of the Test Duration

(Tests on Copper and Bronze VB-24)

Mercaptan Sulfur Content of Original Fuel, wt. %	Test Time at 60°C, hrs: 25 — Mercaptan Sulfur Content, wt. %	25 — Weight Loss of Strip, gm/m²	50 — Mercaptan Sulfur Content, wt. %	50 — Weight Loss of Strip, gm/m²	75 — Mercaptan Sulfur Content, wt. %	75 — Weight Loss of Strip, gm/m²	100 — Mercaptan Sulfur Content, wt. %	100 — Weight Loss of Strip, gm/m²	150 — Mercaptan Sulfur Content, wt. %	150 — Weight Loss of Strip, gm/m²	200 — Mercaptan Sulfur Content, wt. %	200 — Weight Loss of Strip, gm/m²
Copper												
0,008	0,008	absent	0,005	0,20	0,003	0,75	absent	3,15	absent	3,00	absent	3,00
0,016	0,016	*	0,016	absent	0,015	0,20	0,014	0,50	0,014	0,50	0,014	0,70
0,015	0,015	*	0,013	0,75	0,012	2,34	0,007	4,57	absent	7,32	absent	7,30
0,025	0,025	*	0,025	absent	0,025	absent	0,024	0,3	0,024	0,60	0,024	0,80
0,025	0,025	*	0,022	1,73	0,020	3,82	0,015	6,20	0,001	10,85	absent	12,6
0,053	0,050	1,29	0,049	4,15	0,044	3,17	0,039	10,30	0,030	17,08	*	20,0
Bronze VB-24												
0,004	absent	2,34	absent	3,13	absent	3,13	absent	3,08	absent	2,84	absent	2,5
0,016	0,014	2,81	0,009	5,52	0,005	7,10	*	9,60	*	9,77	*	8,95
0,015	0,012	2,01	0,008	4,37	0,003	7,03	*	8,74	*	8,34	*	8,30
0,025	0,022	2,56	0,019	4,52	0,015	6,95	0,007	10,3	*	13,62	*	12,70
0,025	0,022	2,61	0,019	5,23	0,010	7,92	0,004	12,30	*	12,40	*	11,55
0,053		3,12	-	5,2		9,03	—	14,11	-	20,2		20,00

gelatinous deposits on the springs and a sharp decrease in the mercaptan sulfur content of the fuel. The chromate passivation of the cadmized springs exerted a protective action but did not completely prevent the formation of the gelatinous deposit on the springs when tested in this fuel.

Fuel TS-1, containing 0.01% mercaptan sulfur, causes no formation of gelatinou

Table 4

Weight Loss of Cadmized Springs (gm/m^2) during the Test

Fuel	Mercaptan Sulfur Content of Original Fuel, %	Test Conditions for Cadmized Springs					
		Unpassivated			Passivated		
		a)	In Fuel Over a Water Cushion	In Fuel Shaken with Water	a)	In Fuel Over a Water Cushion	In Fuel Shaken with Water
TS-1 (GOST 4138-49)	0,002	0,97	4,10	3,44	Absent	0,23	0,90
TS-1				Absent			
TS-1	0,01	–	27,00	40,00	0,70	3,83	9,26
TS-1	0,026	8,44	106,60	106,77	9,62	13,57	71,83
T-2	0,011	1,66	6,01	35,52	0,9	0,38	1,20

a) In unmoistened fuel

deposits in tests on cadmized springs in unwatered fuel, and very small amounts of deposits in tests in fuel watered by shaking with water.

The loss of weight of passivated cadmized springs tested in this fuel is extremely slight, and the content of mercaptan sulfur in the fuel remains practically unchanged.

Thus, under rather severe test conditions, when cadmized springs are tested in TS-1 fuel containing 0.01% mercaptan sulfur, chromate passivation of the springs reliably protects the cadmium coating and prevents the formation of gelatinous deposits even when the fuel is strongly moistened (fuel with suspended water). Under the test conditions, the corrosiveness of fuel T-2, with 0.01% mercaptan sulfur, is similar to that of fuel TS-1 with the same mercaptan sulfur content. In tests with

springs in a fuel free of mercaptan sulfur, no formation of gelatinous deposits was observed.

Obviously the weight loss of the springs and the formation of gelatinous deposits takes place as a result of the interaction of cadmium with the mercaptans of the fuel (directly or by way of intermediate products) forming cadmium mercaptides. The weight loss is in good agreement with the data on the decrease in the mercaptan sulfur content of the test fuel.

The gelatinous precipitate removed from the cadmised springs consists of 71.5% fuel and 28.5% cadmium mercaptides. The following percentage data were found on determination of the elementary composition of the cadmium mercaptides isolated from the precipitate:

Carbon	46.7
Hydrogen	8.5
Sulfur	16.3
Cadmium	28.5
	100.0

It will be easily seen that the relation between the sulfur content and the cadmium content of the separated mercaptides is close to theoretical. To demonstrate the presence of cadmium mercaptides in the gelatinous precipitate formed, the latter was treated with 50% sulfuric acid, and the free mercaptans were separated. In order to study in more detail the influence of water on the formation of the gelatinous deposits on the cadmised parts of fuel pumps operating on mercaptan-containing fuels, additional experiments were run. Specimens of metallic cadmium were taken for the test in the form of cylinders 100 mm in length and 6 - 7 mm in diameter. Some of the cadmium specimens were machined before the test, to remove the cadmium oxide from their surfaces. The cadmium specimens were tested in TS-1 fuel with 0.04% mercaptan sulfur under the following conditions: in fuel first dried with calcium hydride, i.e., practically free even of dissolved water; in fuel first

shaken with water and stored over a water layer.

The cadmium specimens were tested for three months at room temperature in gl flasks without access of air. In the moistened fuel, the formation of a large amount of gelatinous deposits on both cadmium specimens was observed as early as t following day.

In the dehydrated fuel, the character and rate of formation of the gelatinou deposits was entirely different. On cadmium specimens from whose surface the cadmium oxide had been removed, the gelatinous deposits appeared in the form of isolated points only on the tenth day of the test. During the next two months, the amount of these deposits increased slowly, and only toward the end of the third month did it increase sharply. On the cadmium specimens coated with cadmium oxide traces of deposits appeared only 2.5 months after the beginning of the tests.

Parallel with the tests of specimens of metallic cadmium, we ran the followi experiments under similar conditions: To the fuel TS-1, first dehydrated with calcium hydride, small amounts of synthetically prepared hydrated cadmium oxide we added. The hydrated cadmium oxide for the experiments was either air-dried or moist. In the experiments with the moist hydrated cadmium oxide, the formation of gelatinous deposits was observed on its surface on the day following the beginning of the test. The quantity of these deposits rapidly increased. In the experiment with the air-dried hydrated cadmium oxide, no gelatinous deposits could be detect on its surface during the entire test. When these experiments were run, the merca tan sulfur in the fuel samples was determined before and after the test. Table 5 gives the results.

It will be seen from these data that, in the dehydrated fuel, the hydrated cadmium oxide reacts considerably faster with the mercaptans of the fuel than metallic cadmium does. The presence of water in fuel containing mercaptans accel ates the reaction between the mercaptans of the fuel and the metallic cadmium, as well as the rate of formation of the gelatinous deposits.

The formation of the gelatinous deposits on cadmium coatings, on contact with fuels containing mercaptans, may perhaps pass through the intermediate stage of formation of hydrated cadmium oxide.

Table 5

Measurement of Mercaptan Content in Fuels during the Test

(Mercaptan Sulfur in Original Fuel, 0.04%)

Specimen of Cadmium	Mercaptan Sulfur in Fuel after Test, %	
	In Fuel Dried with Calcium Hydride	In Fuel Moistened by Shaking with Water
Cadmium without oxide film	0.016	0.002
Cadmium with oxide film	0.026	0.002
Air-dried hydrated cadmium oxide	0.001	-
Moist hydrated cadmium oxide	0.002	-

1. The corrosion of copper and bronze VB-24 by fuels prepared from sulfur-bearing crudes is due primarily to the presence of mercaptans in the fuel. Fuels free from mercaptans show practically no corrosive action on copper and bronze VB-24.

2. The presence of up to 0.002% of elementary sulfur in the mercaptan-containing fuel TS-1 does not intensify the corrosive action of this fuel on bronze VB-24 but increases it sharply with respect to copper.

3. Fuel T-2, which is a wide cut containing more mercaptans than fuel TS-1, has a corrosive action on copper. The fact that fuel T-2 has a greater tendency to corrode copper is explained by the considerably greater corrosiveness of the low-molecular mercaptans contained in the 60 - 130°C fraction of fuel T-2.

4. The basic cause responsible for the formation of gelatinous deposits on cadmized parts immersed in fuels TS-1 and T-2 from sulfur-bearing crudes is the

watering of the fuels in the presence of mercaptan sulfur.

5. With increasing content of mercaptan sulfur in the fuel (over 0.01%) the amount of gelatinous deposits on cadmized parts sharply increases.

6. The chromate passivation of cadmized parts increases their resistance to the corrosive action of mercaptans and completely prevents the formation of gelatinous deposits on cadmized parts in fuels TS-1 and T-2 with a mercaptan sulfur content not over 0.01%.

On the basis of this work it has been established that of all the metallic materials used in manufacturing parts for fuel pumps, cadmium coatings are most subject to the action of mercaptans. In this connection, the mercaptan sulfur in fuels TS-1 and T-2 should not exceed 0.01%.

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ORGANIC SULFUR COMPOUNDS IN FUELS AS CORROSION INHIBITORS FOR COPPER AND ITS ALLOYS

by

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The corrosive action of fuels designed for use in gas-turbine engines is an important index of their quality. In the presence of sulfur compounds there is a considerable weight loss of copper or its alloys, of which numerous parts of the fuel system of such engines are made (Bibl.1 - 7).

A more careful study of the question revealed that not all sulfur compounds present in fuels have a tendency to corrode metals (Bibl.8). It was established that elementary sulfur and the mercaptans belong to the unconditionally corrosive compounds (Bibl.9, [illegible]). But the earlier generalization for all mercaptans also proved inaccurate. The mercaptans of aliphatic structure do have strong corrosive properties with respect to copper and its alloys. As for mercaptans of aromatic structure, they were found to exhibit no corrosive activity at temperatures up to 120°C. The corrosive activity of a fuel decreases to zero as the thiol group in the aromatic mercaptans present approaches a ring structure. For example, α-thionaphthol and dithioresorcinol, when present in large amounts in fuels, will not corrode bronze, whereas nonylmercaptan is a powerful corrosive agent with respect to this metal.

Tables 2 and 1 give a characterization of the corrosive action of elementary

Table 1

Corrosive Action of White Spirit in the Presence of Elementary Sulfur

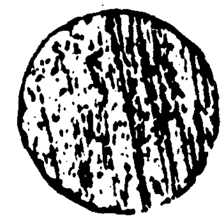
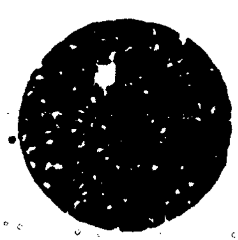
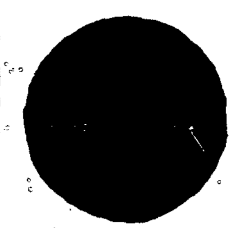
Concentration of Elementary Sulfur, %	Corrosion, gm/m^2	Deposits on Bronze, gm/m^2	Surface of Bronze, Magnification 80 ×
Without elementary sulfur	0	0,3	
0,00[illegible]	3,5	1,1	
0,006	5,3	4,5	
0,008	9,0	8,8	

Table 2

Corrosive Activity of White Spirit in the Presence of Mercaptans

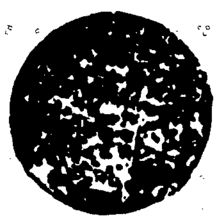
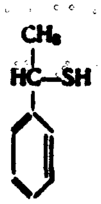
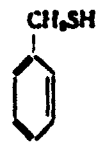
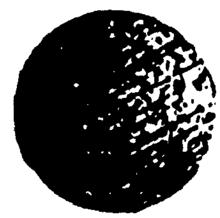
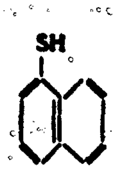
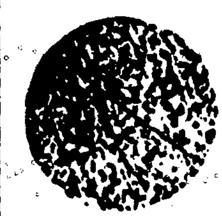
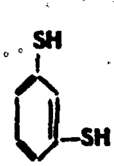
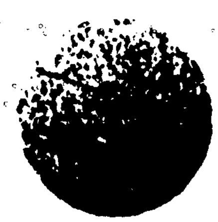
Mercaptans		Corrosion, gm/m^2	Deposit on Bronze, gm/m^2	Surface of Bronze, Magnification 80 ×
Name and Concentration (%)	Formula			
Without Mercaptans		0	0	
Nonylmercaptan (0.045)	$CH_3(CH_2)_8SH$	2,6	8,2	
Decylmercaptan (0.045)	$CH_3(CH_2)_8CH_2SH$	2,3	6,3	
α-Phenylethylmercaptan (0.045)		2,2	5,0	

Table 2 (continued)

Mercaptans		Corrosion, gm/m^2	Deposit on Bronze, gm/m^2	Surface of Bronze, Magnification 80 ×
Name and Concentration (%)	Formula			
Benzylmercaptan (0.045)		1,9	4,3	
Thiophenol (0.530)		0,8	1,5	
α-Thionaphthol (0.530)		0,2	0	
Dithioresorcinol (0.530)		0	0	

sulfur and mercaptans with various chemical structures on antimony-bearing bronze.

Further study of the sulfur compounds with various chemical structures permitted the conclusion that, among the sulfur-containing compounds in fuels, the corrosive compounds and inert compounds may also be accompanied by compounds with a protective anticorrosive influence on the metal.

It was noted that bronze strips after a 6-hr test at 120 - 150°C and certain fuels of various composition and purpose (for example, T-1, Baku straight-run kerosene, and cracked kerosenes of certain sulfur-bearing crudes) become coated with a shiny film of steely or golden color. The film is weak and can be removed mechanically. Underneath the film, the metal has an undamaged and well preserved surface. The metal loss in this case is nil or negligible.

It was obvious that we had to do with a protective film formed and renewed under elevated temperature conditions as a result of chemical interaction between certain compounds present in the fuel in very small amounts and the metal.

Table 3 gives the results of a test with antimony-bearing bronze in several fuels.

The bronze protected by such a film does not become corroded and, consequently, does not lose weight. No adhesive deposits are formed on the metal surface. Moreover, the presence of the film on the metal excludes the catalytic influence of copper under elevated temperature conditions, in the presence of atmospheric oxygen, on the unstable part of the fuel, and as a result, the amount of deep oxidation products formed as insoluble sediments sharply decreases.

It was noted that in certain cracked kerosenes, in which the film was not formed on the metal after addition of small amounts of nitrogen-containing compounds, a shiny film of golden or steely color did appear on the metal, and the corrosion of the bronze, together with the deposits, dropped to very low values. Such an effect was accomplished at 150°C for the cracked kerosene of the Moscow and Kuybyshev refineries.

The cause of the film formation on bronze (this phenomenon was observed on bronzes of various grades) was apparently the presence of compounds containing sulfur and nitrogen.

A somewhat greater clarity was obtained on studying certain individual compounds.

Table 3

Corrosive Activity of Certain Fuels on Antimony-Bearing Bronze

Duration of Test 6 hrs

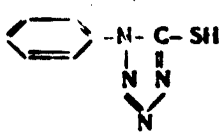
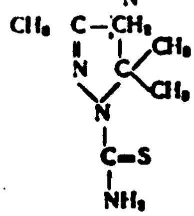
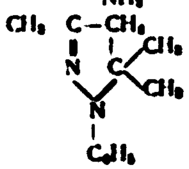
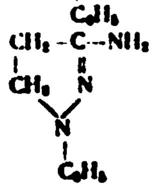
Fuel and Its Characterization	Corrosion gm/m^2	Deposit on Metal gm/m^2	Remarks
Test Temperature 120°C			
TS-1 with 0.045% mercaptans . .	7.1	1.0	Porous, corroded metal surface
Cracked kerosene from Moscow refinery with 0.94% sulfur. . .	5.8	0.9	Same
Cracked kerosene from Kuybyshev refinery with 0.66% sulfur . .	0	0.1	Shiny film of steely color
Cracked kerosene from Saratov refinery with 0.51% sulfur. . .	0	0.2	Shiny film of golden color
TS-1 with 0.10% sulfur.	0.1	0	Same
Straight-run kerosene with 0.10% sulfur	0.0	0.5	Same
Test Temperature 150°C			
TS-1 with 0.045% mercaptans . .	7.5	1.2	Porous, corroded metal surface
Cracked kerosene from Moscow refinery with 0.94% sulfur. . .	6.4	1.0	Same
Cracked kerosene from Kuybyshev refinery with 0.66% sulfur. . .	1.1	2.2	Same
Cracked kerosene from Saratov refinery with 0.51% sulfur. . .	0	0.2	Shiny film of golden color
TS-1 with 0.10% sulfur.	0.3	0.3	Same
Straight-run kerosene with 0.10% sulfur	0.3	0.5	Same

We had available 1-phenyl-5-mercaptotetrazole and individual pyrazolines, synthesised at Moscow State University at the laboratory of A.P.Terent'yev: 1-thiocarbamide-3,5,5-trimethylpyrazoline, 1-phenyl-3,5,5-trimethylpyrazoline, and 3-amino-1-phenylpyrazoline.

These compounds were added to fuel T3-1, which was highly corrosive because of the presence of a considerable amount of mercaptans (0.045%). The 1-phenyl-5-mercaptotetrazole was added to the fuel in an amount of 0.005%, and the remaining

Table 4

Corrosive Activity of Fuel in Presence of Individual Hydrocarbons

Addition	Formula	Corrosion of Bronze gm/m^2	Deposit on Bronze gm/m^2	Precipitate Insoluble in Fuels, mg/100 mg
Without additives		7,1	1,6	17,1
1-phenyl-5-mercapto-tetrazole (0.005%)		0,3	0,3	2,8
1-thiocarbamide-3,5,5-trimethyl-pyrazoline (0.01%)		0,5	0,3	1,5
1-phenyl-3,5,5-tri-methylpyrazoline (0.01%)		5,6	0,8	0,7
4-amino-1-phenyl-pyrazoline (0.01%)		7,0	0,5	1,0

compounds in an amount of 0.01% each. The fuel was then tested for its tendency to corrode antimony-bearing bronze under standard conditions (6 hrs, 120°C).

Table 4 gives the results of the tests.

The formation of a glossy film was observed on testing a fuel with 1-phenyl-5-mercaptotetrazole and 1-thiocarbamide-3,5,5-trimethylpyrazoline. Such a film was not observed in the other cases.

From the data given in Table 4 one may, with a certain amount of caution, draw a preliminary conclusion.

The sharp decrease in the amount of insoluble sediment in the fuel can be explained as due to a "coating" of the bronze surface by the film, as a result of which the catalytic action of copper on the oxidation process of the fuel mercaptans and other unstable components was prevented.

In this connection, the amount of adhesive deposit on the metal sharply decreased. Better results in corrosion prevention and the formation of a protective film were shown by compounds which, in general, consisted of a heterocyclic ring, characterised by the presence of several nitrogen atoms in the ring, and of sulfur. The nitrogen atoms are directly linked to each other, while the sulfur is attached to the ring in the form of a thiol group or over a double bond. Such a heterocycle may exist in combination with the aromatic ring.

Of course, these data are far from sufficient to allow the assertion that the formation of a protective film on bronze is due only to the presence of compounds of this structure in the fuel. However, in connection with the complexity of the question, this assumption was adopted as a preliminary hypothesis, in view of the fact that such compounds may, in principle, be present in fuels in small amounts.

A certain clarification may be achieved by studying the non-hydrocarbon composition of the fuels.

The asphalt portion of the cracked kerosenes produced from Baku and Eastern crudes was separated chromatographically on silica gel. These asphaltic substances were characterised by high nitrogen, sulfur, and oxygen. The portion of the asphaltic substances was treated with a 7% alcoholic alkali solution and vacuum-distilled. Thus, we were dealing with the total asphalt and its neutral portion which amounted to 93 - 95% of the total.

Since the total asphalt compounds had been treated with an alkaline solution t obtain the neutral compounds, we had a right to consider that no compounds with a

thiol group could have remained in the neutral portion. Yet, the neutral portion of the asphaltic compounds was likewise characterized by a high sulfur and nitrogen content. Table 5 gives the elementary composition of these compounds.

Table 5

Elementary Composition of Asphaltic Substances in Fuels, %

Cracked Kerosene	C	H	S	N	O (by Difference)
Baku refinery	80,34	9.41	0,90	2.73	6,57
Moscow refinery	77,41	9,56	3,63	1,13	8,27
Kuybyshev refinery	75,13	9,33	5,10	1,09	9,35
Saratov refinery	77,30	9,81	4,11	1.23	7.55

To test the hypothesis that the asphaltic substances of the fuels contain sulfur and nitrogen-bearing compounds of heterocyclic structure, in the presence of which a protective film is formed at elevated temperatures on bronze, we ran tests

Table 6

Effect of Total Asphaltic Compounds from Cracked Kerosenes on the Formation of Glossy Films on Bronze at 120°C

Total Asphalts Added to Fuel TS-1	%	Corrosion of Bronze gm/m^2	Deposits on Bronze gm/m^2	Surface of Metal
No addition	—	7,1	1,1	Porous, corroded
Cracked kerosene from Baku refinery	0,02	0,8	0,4	
Cracked kerosene from Moscow "	0,01	1,8	0,9	Golden film
Cracked kerosene from Kuybyshev "	0,01	1,0	0,2	
Cracked kerosene from Saratov "	0,01	1,3	0,8	
Cracked kerosene from Kuybyshev " *	0,01	0,3	0,2	

* At 150°C

of the most corrosive fuel, TS-1, with added asphalts from cracked kerosenes. The test conditions were the same as those already described: testing time 6 hrs, temperature 120 and 150°C, bronze of various grades.

The testing of fuel mixed with 0.01 - 0.02% of neutral asphalts, separated from the cracked kerosenes produced by the Moscow, Kuybyshev, and Saratov refineries showed that although the metal loss and the deposit on the metal decreased to about half, no glossy film was formed.

An entirely different picture was observed when certain total asphalts, not treated with alkali, were added. In their presence, the formation of a shiny golden-colored film on the surface of the bronze was observed (see Table 6).

Conclusions

Based on the data obtained, the following preliminary conclusions may be drawn, which will be refined as the work continues.

1. The non-hydrocarbon part of certain fuels contains compounds which, in very small amounts, are able to interact with copper and copper alloys, forming a shiny protective film which prevents the corrosion of metal, and also its catalytic action on the unstable portion of the fuel in an oxidizing medium at high temperatures.

2. There is reason to believe that these compounds are of heterocyclic structure, with one nitrogen atom or with several nitrogen atoms linked to each other. The thiol group or sulfur atom is attached to the carbon of the ring. The heterocyclic ring may be conjugated with the benzene ring.

3. The effectiveness of such compounds in the asphaltic portion of a fuel depends on their amount, on the presence of various other compounds which are corrosive or, by virtue of their inertness, simply lower their concentration, and also depends on the temperature conditions under which the process takes place.

4. We have obtained compounds which, when forming part of corrosive fuels, are able to form a "protective" film on the surface of copper or its alloys. This will permit the use of a larger assortment of crudes for the production of fuels than is the case today.

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THE EFFECT OF ORGANIC SULFUR COMPOUNDS ON THE LOW-TEMPERATURE PROPERTIES AND OXIDIZABILITY OF KEROSENE-GASOIL FRACTIONS

by

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The increasing use of sulfur-bearing fuels and the experience accumulated as to their peculiarities, have raised many questions that need profound study.

The specific nature of Diesel fuels produced from Ural-Volga crudes is explained by their chemical composition, which is characterized by a high content of paraffinic and aromatic hydrocarbons and a relatively high content of sulfur compounds, which reaches 5.- 7%.

The study of the effect of the concentration and structure of sulfur compounds on the low-temperature properties and oxidizability of the fuels containing such compounds occupies an important position in solving the problem of a rational utilization of sulfur-bearing fuels.

Pumping Quality of Fuels

The low-temperature properties of Diesel fuels are of interest to practical workers primarily with regard to their pumping quality. Pumping quality is a very important parameter, since the supply of a precisely predetermined amount of fuel to the combustion chamber of a Diesel engine is one of the fundamental conditions for its stable and uninterrupted operation. The problem of pumping quality for most

Diesel fuels arises only in the region of temperatures below 0°C. Being a function of chemical composition, the pumping quality of dry fuels, from the physicochemical point of view, may be characterised by their viscosity, pour point and cloud point. In evaluating the concept of pumping quality, one must distinguish pipe pumping quality and pumping quality through the filters of the engine fuel system. Pipe pumping quality is a function of the fluidity of a fuel at low temperatures and may

Table 1

Low-Temperature Properties of Eastern Diesel Fuels

Parameter	Fuel					
	a)	TU 305-42	DZ-TU 569-55	VTU 488-53	Experimental with NKZ	GOST 4749-49 (Caucasian)
Boiling range, °C .	200 360	200 300	170 190	230 370	215 350	300 350
Cloud point, °C . .	5	6	38	7	4	11
Pour point, °C. . .	14	15	32	13	19	35
Wax content (solid hydrocarbons) by Zalosetskiy-Galand, % of fuel	0.68	1.02	Absent	0.84	1.08	Absent
Aromatic hydrocarbons, %.	21.3	31.76	3.3	32.1	38.6	14.8
Sulfur, %	1.0	1.08	0.34	0.76	1.25	0.15

a) Krasnokamsk fuel mixed with other fuels from Eastern crudes

be characterised by its viscosity and pour point. The cloud point, fixed as the instant of crystallization and precipitation of solid hydrocarbons from a fuel, is unsuitable for estimating pumping quality through pipes. To estimate the pumping quality through filters, the cloud point is very important characterising, as it does, the state of the fuel at which the throughput of the filter elements may decrease. Diesel fuels with high naphthenic or aromatic hydrocarbons and low methane hydrocarbons, including hydrocarbons which are solid at low temperatures, are rather

well pumped through pipes and through the filter elements of an engine. They are usually characterized by low pour and cloud points. For low-sulfur fuels, the basic criterion which determines the pumping quality is the content of solid hydrocarbons, which is reflected in the pour point and the cloud point. The situation for sulfur-bearing fuels is different. The low-temperature properties of sulfur-bearing Diesel fuels, with 5 - 8% of polar molecules of sulfur compounds, depends not only on the content of solid hydrocarbons but also on the content of sulfur compounds, and apparently also on their structure.

Table 1 gives the low-temperature properties of Diesel fuels and their content of sulfur and aromatic hydrocarbons.

It is obvious that the cloud and pour points of the samples studied depend not only on the content of solid hydrocarbons but also on that of sulfur compounds. For example, the experimental Diesel fuel with NKZ, containing 1.68% solid hydrocarbons and 1.25% sulfur, solidifies at -19°C, whereas the Diesel fuel per VTU 488-53, containing 0.84% wax (after Zalozetskiy) and almost the same amount of aromatic hydrocarbons as the experimental fuel, but also containing 0.76% of bound sulfur, solidifies at -13°C. A certain influence of aromatic hydrocarbons, owing to the presence of a field of force which apparently influences the surrounding substance, is also not excluded. This may be noted in comparing the properties of Krasnokamsk fuel with fuel per TU 305-42. These fuels, which have almost the same pour and cloud points, contain almost equal amounts of sulfur compounds but differ considerably in content of solid and aromatic hydrocarbons. Apparently, the polar sulfur compounds and condensed aromatic hydrocarbons, like the asphaltic substances, favor the appearance of globules of solid hydrocarbons and, preventing the formation of a structure, retain them in the fuel in the suspended state. From this point of view, it can be postulated that a fuel with the same amount of solid hydrocarbons should have a better pumpability through pipes at higher contents of sulfur compounds and aromatic hydrocarbons. Obviously, the effect of sulfur compounds is greater than

that of the aromatic hydrocarbons.

However, pipe pumping quality is of secondary importance in Diesel operation. It is far more important for operating purposes to have a fuel with good pumping

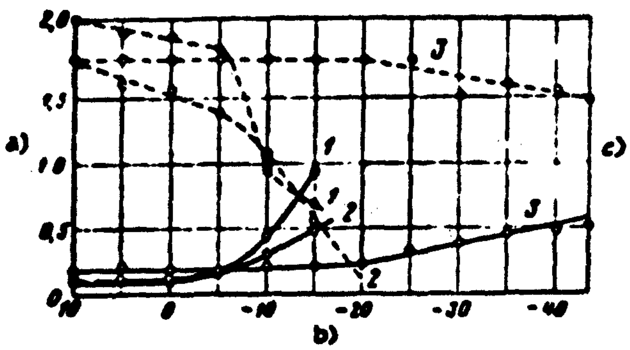

Fig.1 - Discharge and Pressure Versus Temperature in Pumping Diesel Fuels on a Laboratory Pumping Stand

1 - Diesel fuel per GOST 305-42; 2 - Krasnokamsk Diesel fuel; 3 - Diesel per DZ-TU 569-55; - - - Discharge, ltr/min; —— Pressure before filter, kg/cm^2

a) Pressure before filters, atm; b) Temperature, °C; c) Discharge, ltr/min

quality through the filter elements. Diesel fuels produced from Eastern crudes, containing an appreciable amount of solid hydrocarbons and of sulfur compounds and aromatic molecules that favor their aggregation, possess a poorer low-temperature pumping quality for filter elements. The experimental evaluation of the pumping quality of sulfur-bearing Diesel fuels,made on a laboratory stand with a filter taken from a 2D-6 engine, with felt filter elements, has shown that the pumping of the experimental samples falls sharply at pumping temperatures corresponding to the cloud point of the test samples. On this stand, we estimated the pressure rise in front of the filter and the filtering power of the filter when constant pressure was maintained in front of it. The experiments showed a sharp increase in pressure before the filters and a decrease in filtering power, noted several minutes after the temperature of the fuel had dropped to the cloud point. Figures 1 and 2 show the

results of the experiments.

In the light of the above it is not without interest to recall certain other features of sulfur-bearing Diesel fuels that have recently been discovered. In some cases, after prolonged storage of sulfur-bearing Diesel fuels in tanks and reservoirs, at temperatures above 0°C, a layer of solid porous wax was found floating on the surface. No similar phenomenon was encountered in the storage even of sulfur-free summer fuels with a considerable amount of solid hydrocarbons.

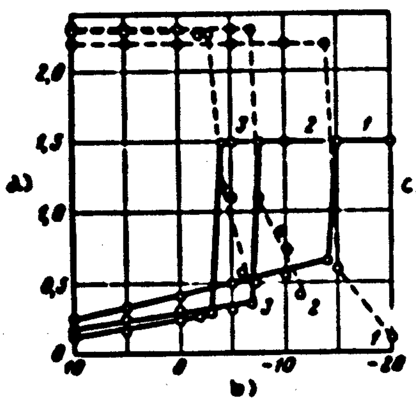

Fig.2 - Curves of the Temperature Dependence of the Discharge and Pressure in Pumping Fuels on a Laboratory Pumping Stand

1 - Diesel fuel per GOST 4749-49;
2 - Diesel fuel per VTU 488-53;
3 - Diesel fuel from Novo Kuybyshev refinery; S = 1.25%;
- - - Discharge, ltr/min;
—— Pressure before filter, kg/cm²

a) Pressure before filter, atm; b) Temperature, °C; c) Discharge, ltr/min

In B.V.Losikov's opinion, this phenomenon is due to the formation of conglomerates of solid hydrocarbons on draining the cold fuel; such conglomerates are not interconnected, owing to the influence of the sulfur compounds, and are thus attracted to the surface by the air entrained on addition or removal of fuel. The conglomerates of solid hydrocarbons floating on the surface freeze at a low temperature, separating the fuel, and form a solid porous cake floating on the surface. A preliminary experimental check performed by a brief blowthrough of the experimental fuel with NKZ, containing 1.65% of wax (after Zalosetskiy) and 1.25% of sulfur, which had been cooled to -12°C, followed by further cooling for 6 - 7 hrs to -20 and -30°C, showed that foam, which did not disintegrate at a temperature of +15°C, collected on the surface of the fuel. The porous mass removed was melted and examined for wax (after Zalosetskiy, Bibl.1) and pour point. We found that the

wax after Zalozetskiy in the melted foam was 4 - 6 times as high as its content in the fuel, and that the pour point ranged from 20 to 22°C (the pour point of the fuel was -19°C).

Chemical Stability

The chemical stability of fuels characterizes their power to maintain their composition without change during prolonged storage in contact with air under various climatic conditions. The resistance of petroleum products to the action of atmospheric oxygen, as shown by many investigators (Bibl.2 - 5), depends on their molecular weight and chemical composition.

No reliable data are today available on the behavior of Diesel fuels of varying chemical composition during prolonged storage, in various holders and packages.

To elucidate the effect of the concentration of organic sulfur compounds, we ran experiments on the artificial aging of sulfur-bearing Diesel fuels in the presence of iron and copper. The kinetics of the oxidative processes during their initial stage was investigated.

Three samples of Romashkin gasoil and two specimens of Tuymazy gasoil were oxidized. To elucidate the influence of organic sulfur, it was necessary to have fuels with the same hydrocarbon composition and different content of sulfur compounds. For this purpose, the original Romashkin gasoil, containing 0.62% sulfur (sample No.1), was twice desulfurized. After the first superficial desulfurizing over silica gel, the gasoil contained 0.32% sulfur whereas after its oxidation by H_2O_2 at 60°C, followed by chromatographic separation of the oxidation products, it contained no sulfur (sample No.3). The Tuymazy specimens were straight-run distillates, original and after hydrofining. The original distillate contained 0.96% sulfur, and the hydrofined distillate 0.04%. Table 2 gives the characteristics of the gasoils studied.

The samples of Romashkin gasoil were oxidized in a flow plant at 100°C and an

oxygen flow rate of 6 ltr/hr for 10 hrs. In all cases, two parallel oxidation experiments were run under the same conditions. Samples (2 - 3 gm) were taken during the experiments from the product being oxidized, and their acid numbers,

Table 2

Characteristics of Gasoils Studied

Physical and Chemical Properties and Chemical Composition	Romashkin Gasoil			Tuymazy Gasoil	
	Specimen No.			Specimen No.	
	1	2	3	4	5
Boiling range, °C	155-320	156-315	153-320	230-330	224-330
Density, ρ_4^{20} ...	0.8161	0.8158	0.8156	0.8300	0.8292
Refractive index, n_D^{20} ...	1.4540	1.4494	1.4492	1.4682	1.4634
Actual gum, mg/100 ml ...	34	-		5	
Total sulfur, %	0.62	0.32	none	0.96	0.04
Elementary sulfur, %	0.02	Absent		Absent	
Hydrogen sulfide, %		"		"	
Mercaptans, %	0.02	none	none	0.005	none
Sulfides, %	0.24	"	"	0.470	"
Disulfides, %	0.02	0.015	"	0.002	"
Residual sulfur, %	0.32	0.304	"	0.383	0.04
Acidity, mg KOH/100 ml ..	0.2	-	-	1.0	0.9
Aromatic hydrocarbons, %	22	---	-	32	31
Iodine number	0.67	—	—	—	—

peroxide numbers, hydroxyl numbers, and saponification numbers were potentiometrically determined (Bibl.6, 7).

After 10 hrs of oxidation, the actual gum was determined in all samples. The samples of Tuymazy gasoil were oxidized in a glass bulb at 100°C at an air-flow rate of 10 ltr/hr for 1, 3, 6, 9, and 12 hrs. The optical density, which was considered as a function of the accumulation of asphaltic substances, was measured in the oxidized specimens by a photoelectric colorimeter, and the acidity was measured potentiometrically. Figures 3 - 7 give all the experimental results.

Cause of the Difference in the Kinetics of Peroxide Accumulation

On considering the curve of peroxide accumulation for the three samples of

Romashkin gasoil (Fig.3), the substantial difference in their character will be easily noted.*

The accumulation of peroxides during the oxidation of specimen No.1, at least

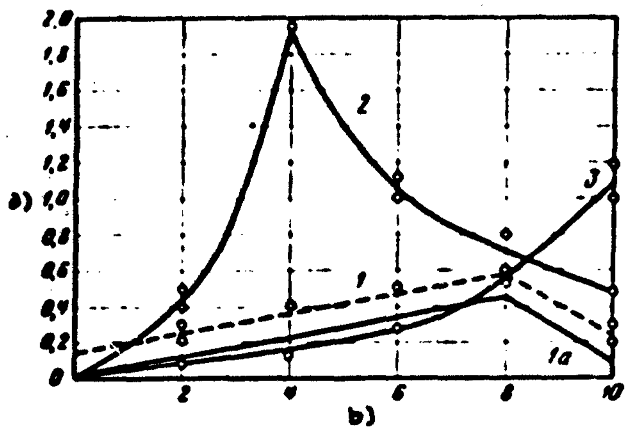

Fig.3 - Variation in Peroxide Numbers with Time
(See Footnote on p.31)

1 and 1a - Sample with 0.62% of sulfur; 2 - 0.32% sulfur; 3 - Desulfurized sample

a) Peroxide number; b) Hours

up to the maximum which occurred after 8 hrs of oxidation, is linear, which is not a characteristic property of autocatalytic processes.

During the oxidation of sample No.2, an inflection in the curve occurred after 4 hrs of oxidation, and the character was clearly autocatalytic, whereas the increase in the amount of peroxides after 4 hrs of oxidation was very rapid.

The accumulation of peroxides in sample No.3 takes place along a curve indicating the autocatalytic course of the process, but less intensely than during the oxidation of sample No.2. During almost 8 hrs of oxidation, the absolute quantity of peroxide on any stage of the oxidation of this sample was less than during the

* Curves 1a in Figs.3 - 6 were obtained by shifting the points of the experimental curves 1 by the initial values (respectively) of the peroxide, acid, and hydroxyl numbers, and the saponification numbers determined in sample No.1 before oxidation.

oxidation of the other gasoil (samples Nos.1 and 2). To judge from the slope of the curve, the mean rate of accumulation of peroxides was higher in sample No.3 than in sample No.1.

If organic sulfur has antioxidant properties, then the increase in the rate of peroxide accumulation with decreasing sulfur content was entirely regular. But the cause of the difference in the character of the kinetic curves of peroxide accumulation remains unexplained. For example, on oxidation of sample No.2 the maximum amount of peroxides is formed, but the inflection of the curve takes place, not after 8 hrs as in sample No.1, but twice as fast. In the case of the desulfurized kerosene (sample No.3) the peroxide accumulation curve has no inflection and is considerably flatter than the curve of sample No.2. The peroxide accumulation curve in sample No.1 is not of autocatalytic character, and the absolute amount of peroxides during almost 7 hrs of its oxidation is higher than that of sample No.3. To explain the difference in the kinetics of peroxide accumulation on oxidation of these samples of gasoil, the following considerations may be proposed: At low concentrations of organic sulfur (sample No.2) peroxide compounds are formed not only by oxidation of the hydrocarbons, but also by oxidation of the sulfur compounds. Subsequently, at a certain stage, on decomposition of the primary oxygen compound of organic sulfur, substances are formed that readily react with the peroxides and in this way decrease their concentration. If the sulfur concentration is high, then the formation of substances readily reacting with the peroxides proceeds rapidly, and their concentration is sufficient; consequently, the hydrocarbon peroxides formed rapidly react with them and have no time to accumulate in the substrate. In this case, the total peroxide concentration is the resultant of two processes. The latter case may be observed on comparing the curves characterising the peroxide accumulation in samples Nos.1 and 2. The curve of the peroxide numbers for sample No.3 has no maximum, which is entirely admissible under the mild conditions of a brief oxidation, even in the absence of antioxidants. The smooth rise in the quan-

tity of peroxides for the desulfurized gasoils indicates the relatively low conversion of the peroxides, if it takes place without interference of extraneous factors. The fact that the rate of accumulation of peroxides in the latter case is higher than during the oxidation of sample No.1, and that in a number of oxidation stages their absolute value is lower than in sample No.1, is explained by the fact that in samples Nos.1 and 2 the sources of peroxide formation are the hydrocarbons and sulfur compounds, while in sample No.3 the only such sources are hydrocarbons.

Kinetics of Formation of Acid Substances

As will be seen from Fig.4, the accumulation of acid substances in all cases is linear. The original samples Nos.2 and 3 had no acidity before oxidation. The acidity of sample No.1 before oxidation was 0.2 mg. For convenience of comparison of the kinetics of oxidation of these samples of gasoil, the second curve (1a) has been constructed, with the original value of the acid number subtracted from all values of the acid numbers found. The slopes of the kinetic curves are different. The smallest slope is formed by the curve of sample 2, the intermediate position is occupied by the curve of desulfurized gasoil, while the highest rate of formation of acid compounds is for the original gasoil. Apparently, the cause for the increase in acidity found on oxidation of specimen No.1 are not only the organic acids formed as a result of the oxidation of hydrocarbons, but also the acid substances formed on oxidation of elementary sulfur and of organic sulfur compounds. The role of elementary sulfur is distinctly mani-

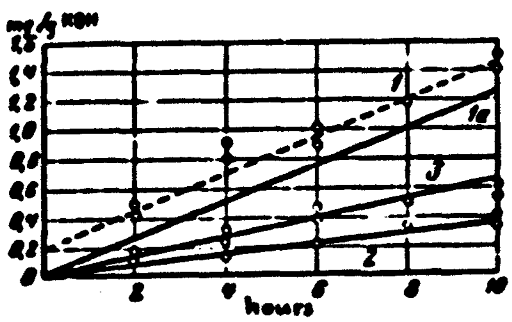

Fig.4 - Kinetics of Variation in the Content of Acid Substances in Samples of Gasoil from Romashkin Crude (See Footnote on p.31):

1 and 1a - Specimen with 0.62% of sulfur; 2 - 0.32% S; 3 - Desulfurized sample

fested if we compare the kinetic curve of the original and desulfurized Romashkin and Tuymazy gasoils. The Tuymazy sulfur-bearing gasoil (Fig.4a) (sample No.4) which

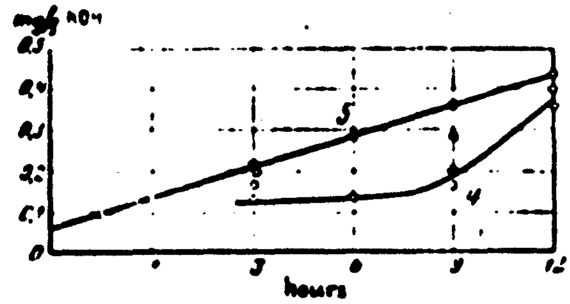

Fig.4a - Variation in Acid Number of Gasoil from Tuymazy Crude before and after Hydrofining

4 - Sample before hydrofining, S = 0.96%; 5 - Specimen after hydrofining, S = 0.04%

did not contain elementary sulfur, had a lower acidity at all stages of oxidation

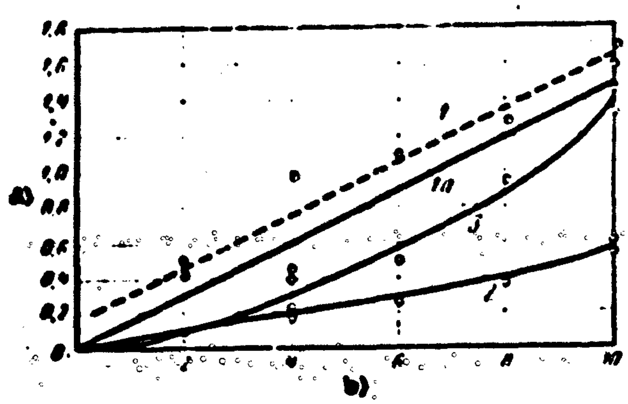

Fig.5 - Kinetics of Formation of Hydroxyl-Containing Substances (See Footnote on p.31):

1 and 1a - Sample with 0.62% S; 2 - 0.32% S; 3 - Desulfurized sample

a) Hydroxyl number; b) Hours

than the desulfurized gasoil of sample No.5.

Kinetics of Formation of Hydroxyl-Containing Substances

In considering the kinetics of accumulation of hydroxyl-containing substances (Fig.5), our attention is struck by the radical difference in the kinetic curve of sample No.1. The accumulation of hydroxyl-forming substances here is linear, which indicates a retarding process, but the rate of their formation is considerably higher than that in sample No.2.

The center curve (sample No.3) has a distinctly autocatalytic character. The rate of formation of hydroxyl-containing substances on oxidation of desulfurized gas oil in the last analysis becomes the highest of all.

The causes of this phenomena are evidently as follows: During oxidation of the desulfurized gasoil, the process proceeds autocatalytically, and the accumulation of hydroxyl-containing substances depends only on the process conditions and the hydrocarbon composition of the test gasoil. The addition of a small quantity of sulfur-containing compounds modifies the character of the conversion of peroxides. The reaction of condensation begins to predominate over the reaction of decomposition, and as a result the absolute quantity and rate of accumulation of hydroxyl-containing substances decreases.

At considerable quantities of sulfur compounds, especially of the sulfide type, an oxidative decomposition of peroxides (Bibl.10), with formation of hydroxyl-containing organic molecules, is apparently possible. This is obviously the cause of the peculiar character of accumulation of these substances during the oxidation of gasoil (sample No.1). It must be noted that also this curve should be shifted in the direction of the abscissa axis, since a small quantity of hydroxyl-containing substances, which we at first neglected, was present in the original sample, even before the beginning of oxidation in the reactor.

Kinetics of Formation of Saponifiable Substances

Saponifiable substances are formed to a considerable extent as a result of the

interaction of acid and hydroxyl-containing substances. It is interesting to note that the character of the curve for sample No.1 (Fig.6) is to some extent connected

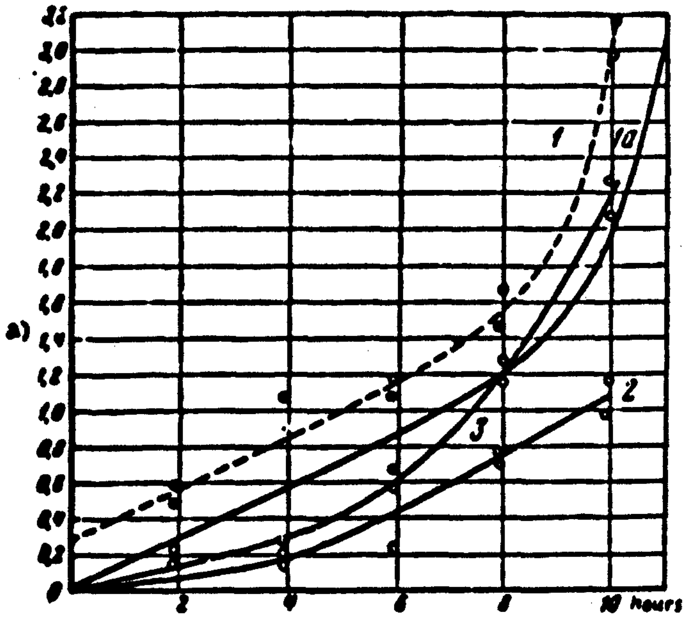

Fig.6 - Kinetics of Variation of Saponifiable Substances (See Footnote on p.31):

1 and 1a - Specimen with 0.62% S; 2 - 0.32% S; 3 - Desulfurized sample

a) Saponification value; b) Hours

with the character of the curve of the hydroxyl numbers for the same gasoil. The linear character of the curve of accumulation of hydroxyl-containing substances exerts an influence on the form of the curves of accumulation of the saponifiable substances. Apparently here, too, the role of the acid compounds formed during oxidation of various compounds is not excluded. It is precisely for this reason that the total quantity of saponifiable substances is maximum for all oxidation stages of sample No.1. The retardation of the reaction of decomposition of the peroxide compounds due to the sulfur compounds during oxidation of sample No.2, which led to a lower content of acid and hydroxyl compounds than in samples Nos.1 and 3, should

naturally lead to lower velocities in the formation of saponifiable substances during the oxidation of gasoil No.2 than during the oxidation of samples Nos.1 and 3.

The kinetics of accumulation of saponifiable substances during the oxidation of the desulfurized gasoil No.3 depends only on its hydrocarbon content and is directly related to the character of the accumulation of acid and hydroxyl-containing substances during oxidation.

Gum Formation

The kinetics of gum formation during the oxidation of Romashkin gasoil was not investigated, owing to the lack of a simple and reliable micro-method of determining

Table 3

Actual Gum in Original and Oxidized Samples of Romashkin Gasoil

Specimen No.	Actual Gum, mg/100 ml	
	Before Oxidation	After Oxidation
1.(S = 0.62%)	34	154
2 (S = 0.32%)	none	143
3 (desulfurised)	none	84

the condensation products; nevertheless, after oxidation of the substrate, we did investigate the actual gum (cf. Table 3). It was found here that the maximum amount of gum was formed in gasoils containing sulfur compounds. This latter circumstance was manifested with particular distinctness in considering the kinetic curves of variation in the optical density of sulfur-bearing and desulfurized Tuymazy gasoils (Fig.7).

Under relatively mild oxidation conditions, the gum formation in gasoil containing 0.04% sulfur was very rapidly retarded and practically failed to proceed at all during 9 hrs of oxidation. On the other hand, the sulfur-containing gasoil progres-

sively accumulates gummy substances. Taking due cognizance of the presence of a certain amount of gum in the original Romashkin gasoil, we may consider that the relatively small amount of sulfur compounds (0.32%) effectively favors the process of conversion of the peroxides, which is directed toward condensation and, consequently, also toward gum formation.

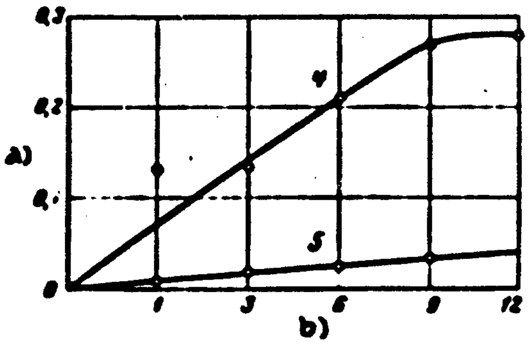

Fig.7 - Kinetics of Variation of Optical Density of Gas Oils from Tuymazy Crude before and after Hydrofining on their Oxidation

4 - Fuel before hydrofining; 5 - Fuel after hydrofining

a) Optical density; b) Hours

Starting out from this, it is possible to postulate that there should exist a "threshold" of sulfur concentration, which, when exceeded, no longer leads to effective gum formation. On the other hand, apparently, for the development of processes of gum formation, a high concentration of sulfur compounds is not necessary, and all that is necessary is that their content shall be sufficient to interact with most of the peroxide compounds formed during oxidation of the hydrocarbons.

Hence it is clear that the value of the "threshold" of gum formation for the concentration of sulfur compounds is dependent on the hydrocarbon composition of the gasoil under study and undoubtedly also on the structure of the sulfur compounds.

<u>The Effect of Gums Contained in the Original Gasoil</u>

In connection with the literature considerations on the antioxidant action of gum-like substances, it is expedient to evaluate their influence on the kinetics and character of the oxidative process.

From a comparison of the kinetic curve obtained by oxidation of sample Nos.1 and 2, and the amounts of actual gum determined in the oxidized samples, it will be

clear that the maximum amount of products of oxidative decomposition appear in the gum-containing sample No.1, and the actual gum found in the degummed and oxidized sample No.2 even exceeds that of the newly formed gum in the oxidized sample No.1.

At the same time, a comparison of the results during the oxidation of the degummed samples Nos.2 and 3 (sulfur-containing and sulfur-free, respectively) convincingly shows the influence of sulfur-bearing substances, but not of gums, on the kinetics of decomposition of peroxides and the process of accumulation of condensation products.

These data prove that the gum-like substances in the original gasoil have no substantial influence on the character and kinetics of oxidation of that gasoil.

Conclusions

1. It has been established that sulfur compounds prevent the autocatalytic development of the oxidative process.

2. The "antioxidative" functions of sulfur-containing compounds consist in their interaction with, and in the products of their oxidation by, peroxide radicals or hydroperoxides of hydrocarbons.

3. By preventing the decomposition of peroxides by the free radicals, and, consequently, the development of oxidative chains, the sulfur compounds accelerate the processes of oxidative polymerization and condensation, as a result of which gum-like substances accumulate. A high concentration of sulfur compounds is not required for an intense accumulation of such gum-like substances. The minimum amount of "sulfur" in gasoil that is permissible from this point of view depends on the chemical structure and relative quantities of the sulfur compounds containing it and on the chemical composition of the gasoil being oxidized.

4. Sulfur compounds at low concentration prevent the formation of acid, hydroxyl-containing, and saponifiable substances which are due to the oxidative decomposition of peroxides. The optimum concentration of "total sulfur" that will prevent an ac-

cumulation of these substances depends on the chemical structure and relative amounts of the sulfur compounds composing it and, apparently, on the chemical composition of the gasoil being oxidised.

5. The gum-like substances contained in the original Romashkin gasoil are not antioxidants, and have no substantial effect on the character or kinetics of its oxidation.

6. The results obtained indicate the need for deep extraction of the sulfur compounds from the kerosene-gasoil fractions. To obtain optimum results, not only on gum formation but also on acidity, however, it is apparently necessary to leave a small amount of sulfur compounds in the gasoils. The optimum quantity of "favorable and preventive sulfur" should first be established for a petroleum product to be hydrofined.

7. The presence of sulfur compounds in waxy petroleum products favors a decrease in the temperature of structure formation.

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Answers to Questions

Question. Which is it that affects the formation of a wax layer on the surface of a fuel, the presence of sulfur compounds, or the chemical composition of the hydrocarbon part of the fuel?

Answer. We can give only a preliminary answer, since this question needs further study. We did find that aromatic hydrocarbons exert an influence, although to a lesser degree than sulfur compounds.